2034
doi:10.1017/S1431927619010900
Microsc. Microanal. 25 (Suppl 2), 2019

Understanding the Structure of $LiMn_2O_4$ by Differential Phase Contrast

S. Calderon V.[1*], J.D. Guimarães[2], R. Ribeiro[1,2], P.J. Ferreira[1,3,4]

[1.] INL - International Iberian Nanotechnology Laboratory, Braga, Portugal.
[2.] Centro de Física and Departamento de Física, Universidade do Minho, Campus de Gualtar, Braga Portugal.
[3.] Materials Science and Engineering Program, The University of Texas at Austin, Austin, USA.
[4.] Mechanical Engineering Department and IDMEC, Instituto Superior Técnico, University of Lisbon, Lisboa, Portugal.
* Corresponding author: secave44@gmail.com

Nowadays, a global revolution in the energy sector is required to counteract the unsustainable pressure on the natural resources. The major challenges in this sector are to efficiently use renewable energy and efficiently storage the energy harvested by eco-friendly methods. In this regard, lithium-ion batteries have been the fastest growing and most promising way of storing energy. However, some drawbacks, such as the voltage and current limits for a safe use, the toxicity of some dopant elements and the loss of capacity due to aging, limit their utilization. $LiMn_2O_4$, for example, is a well-known cathode material due to its ability to exchange Li-ions in a three-dimensional spinel structure. Yet, this material has shown capacity loss, attributed to the dissolution of Mn to the electrolyte. Amos et. al [1] have demonstrated a restructured surface in this material, where a stable surface layer of Mn_3O_4, followed by $Li_{1+x}Mn_2O_4$ subsurface with retention of bulk $LiMn_2O_4$ is formed.

In this context, understanding the structure of $LiMn_2O_4$ is of paramount importance to be able to maximize its storage capabilities, control the safety issues and reduce the capacity loss. Recent advances in scanning transmission electron microscopy (STEM) allow us to observe not only the structure of the materials at atomic level, but also to obtain images proportional to the projected potential [2], the projected electric field [3] and the projected charge distribution [4], by using differential phase contrast technique (DPC). Thus, in this work we use DPC to determine the Li, Mn and O atoms positions, thus providing a novel insight into the structure of $LiMn_2O_4$.

STEM images were acquired in a double-corrected FEI Titan-Themis TEM/STEM, operated at 200kV. Simultaneously, annular dark field (ADF), annular bright field (ABF) and DPC images were obtain from pristine $LiMn_2O_4$ nanoparticles. A segmented annular detector was used to image the in-plane displacement of the transmitted electrons, which is proportional to the projected electric field, while the images proportional to the potential and charge distribution were calculated accordingly to [2,4]. Our results clearly show local regions depleted in Li and the existence of manganese atoms in tetrahedral sites occupying a typical Li atom position, or occupying a free octahedral site in the same column, in agreement with the Mn disproportionation reaction reported for such compound. Simulated DPC-STEM images obtained by the multislice calculations and DFT calculation of the projected potential and electric field were performed to confirm the experimental images. These findings contribute to a better understanding of the mechanisms of lithium and manganese exchange in $LiMn_2O_4$ spinel structures [5].

References:

[1] C.D. Amos et al., Nano Letters **16**(5) (2016), p. 2899-2906.

[2] I. Lazić, E.G.T. Bosch and S. Lazar, Ultramicroscopy **160** (2016), p. 265-280.
[3] N. Shibata et al., Nat. Commun. **8** (2017), p. 15631.
[4] G. Sánchez-Santolino et al., ACS Nano **12**(9) (2018), p. 8875-8881.
[5] The authors would like to acknowledge that this project has received funding from the EU Framework Programme for Research and Innovation H2020, scheme COFUND – Co-funding of Regional, National and International Programmes, under Grant Agreement 713640.

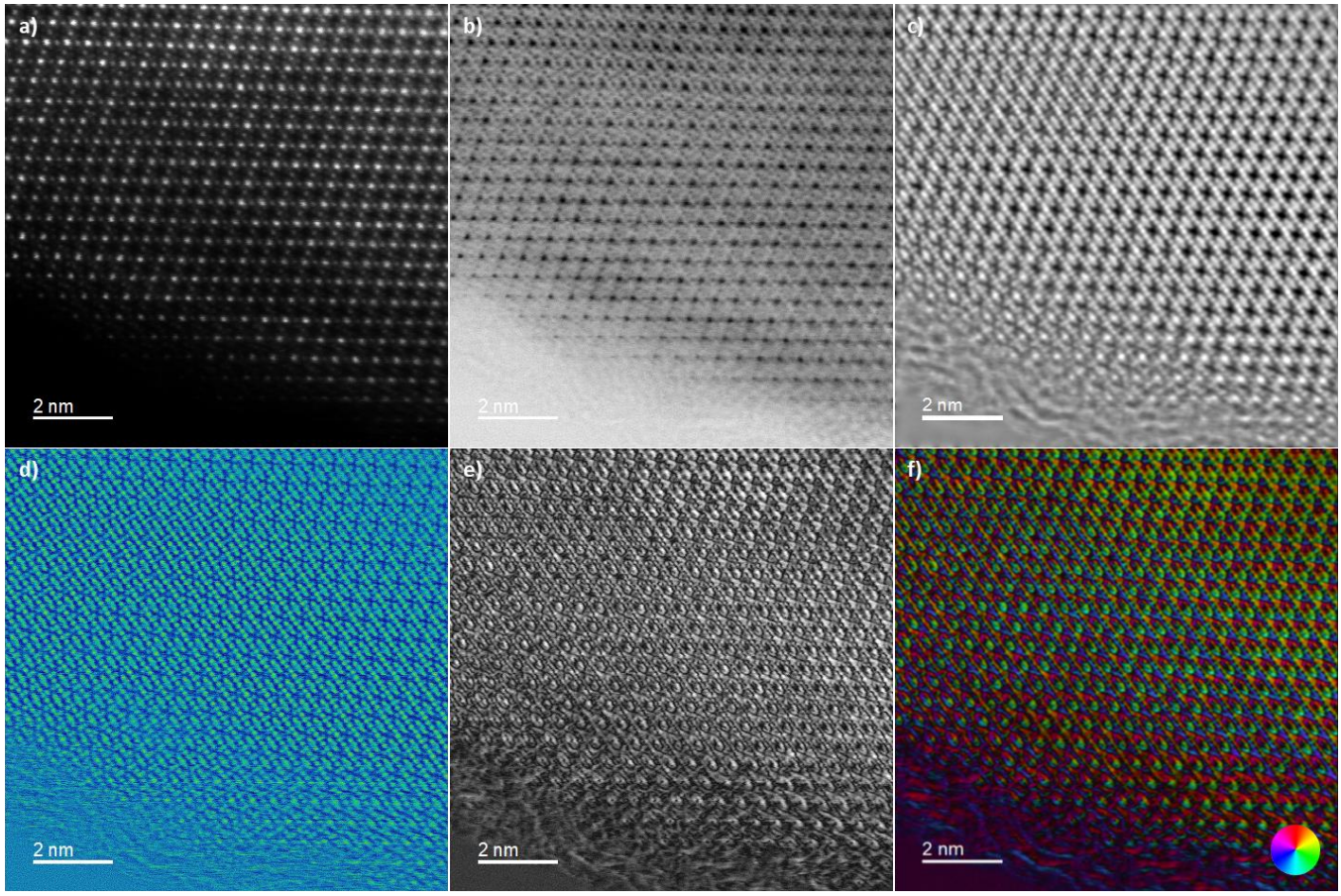

Figure 1. STEM images of $LiMn_2O_4$ along the [011] zone axis a) ADF, b) ABF, c-e) images proportional to the projected c) potential, d) charge distribution, e) electric field, c) charge density distribution and f) electric field direction.

https://doi.org/10.1017/S1431927619010900 Published online by Cambridge University Press